An equation of state *à la* Carnahan-Starling for a five-dimensional fluid of hard hyperspheres

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The equation of state for five-dimensional hard hyperspheres arising as a weighted average of the Percus-Yevick compressibility ($\frac{3}{5}$) and virial ($\frac{2}{5}$) equations of state is considered. This Carnahan-Starling-like equation turns out to be extremely accurate, despite the fact that both Percus-Yevick equations of state are rather poor.

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Although not present in nature, fluids of hard hyperspheres in high dimensions ($d \geq 4$) have attracted the attention of a number of researchers over the last twenty years.[1–14] Among these studies, one of the most important outcomes was the realization by Freasier and Isbister[1] and, independently, by Leutheusser[4] that the Percus-Yevick (PY) equation[15] admits an exact solution for a system of hard spheres in $d =$ odd dimensions. In the special case of a five-dimensional system ($d = 5$), the virial series representation of the compressibility factor $Z \equiv p/\rho k_B T$ (where p is the pressure, ρ is the number density, k_B is the Boltzmann constant, and T is the temperature) is $Z(\eta) = \sum_{n=0}^{\infty} b_{n+1}\eta^n$, where $\eta = (\pi^2/60)\rho\sigma^5$ is the volume fraction (σ being the diameter of a sphere) and b_n are (reduced) virial coefficients. The exact values of the first four virial coefficients are[2,10] $b_1 = 1$, $b_2 = 16$, $b_3 = 106$, and $b_4 = 311.18341(2)$. The fifth virial coefficient was estimated by Monte Carlo integration to be $b_5 \simeq 970$.[1] More recent and accurate Monte Carlo calculations yield $b_5 = 843(4)$ and $b_6 = 988(28)$.[14] The exact knowledge of the virial coefficients b_1–b_4 and in some cases of the Monte Carlo values for b_5 and b_6 has been exploited to construct several approximate equations of state (EOS), several of them being reviewed in Ref. 14.

One of the simplest proposals is Song, Mason, and Stratt's (SMS),[7] who, by viewing the Carnahan-Starling (CS) EOS for $d = 3$[16] as arising from a kind of mean-field theory, arrived at a generalization for d dimensions that makes use of the first three virial coefficients. Baus and Colot (BC)[6] proposed a *rescaled* (truncated) virial expansion that explicitly accounts for the first four virial coefficients. A slightly more sophisticated EOS is the *rescaled* Padé approximant proposed by Maeso *et al.* (MSAV),[12] which reads

$$Z_{\rm MSAV}(\eta) = \frac{1 + p_1\eta + p_2\eta^2}{(1-\eta)^5(1+q_1\eta)}, \tag{1}$$

where $p_1 = (776 - b_4)/36$, $p_2 = (5476 - 11b_4)/36$, and $q_1 = (380 - b_4)/36$. One of the most accurate proposals to date is the semi-empirical EOS proposed by Luban and Michels.[10] These authors first introduce a function $\zeta(\eta)$ defined by

$$Z_{\rm LM}(\eta) = 1 + \frac{b_2\eta\left\{1 + \left[b_3/b_2 - \zeta(\eta)b_4/b_3\right]\eta\right\}}{1 - \zeta(\eta)(b_4/b_3)\eta + \left[\zeta(\eta) - 1\right](b_4/b_2)\eta^2}. \tag{2}$$

Equation (2) is consistent with the exact first four virial coefficients, regardless of the choice of $\zeta(\eta)$. The approximation $\zeta(\eta) = 1$ is equivalent to assuming a Padé approximant [2,1] for $Z(\eta)$. Instead, Luban and Michels observed that the computer simulation data of Ref. 5, $\{Z_{\rm sim}(\eta_i), i = 1, \ldots, 8\}$ [cf. Table I], favor a *linear* approximation for $\zeta(\eta)$ and, by a least-square fit, they found $\zeta(\eta) = 1.074(16) + 0.350(96)\eta$. Another semi-empirical EOS (not included in Ref. 14) was proposed by Amorós *et al.* (ASV):[8]

$$Z_{\rm ASV}(\eta) = \sum_{n=0}^{4} \beta_{n+1}\eta^n + \frac{5\eta_0}{\eta_0 - \eta} + C\eta^4\left[\frac{1}{(1-\eta)^4} - 1\right]. \tag{3}$$

This equation imposes a single pole at the close-packing fraction $\eta_0 = \sqrt{2}\pi^2/30$. The parameters $\beta_n = b_n - 5\eta_0^{-(n-1)}$ are fixed so as to reproduce the first five virial coefficients, while C is determined by a fit to simulation data.[5] By using the presently known values of b_4 and b_5 and minimizing $\sum_{i=1}^{8}[1 - Z_{\rm ASV}(\eta_i)/Z_{\rm sim}(\eta_i)]^2$ one finds $C = 276.88$. Finally, Padé approximants [2,3] and [3,2] have also been considered.[14]

All the previous EOS rely upon some extra information, such as known virial coefficients and simulation data. On the other hand, (approximate) integral equation theories[15] provide the correlation functions describing the structure of the fluid. From these functions one can obtain the EOS, that usually adopts a different form depending on the route followed. As said above, the PY integral equation has an exact solution for a system of hard spheres in odd dimensions. In particular, the analytical expressions of the EOS obtained from the virial route, $Z_{\text{PY-v}}(\eta)$, and from the compressibility route, $Z_{\text{PY-c}}(\eta)$ are known for $d = 5$.[1,4,11,14] Nevertheless, these two EOS are highly inconsistent with each other.[1,14] This inconsistency problem is also present with lower dimensions (except in the one-dimensional case, where the PY theory becomes exact), but to a lesser extent. This led Freasier and Isbister[1] to conclude that

"the PY approximation for hard cores is an increasingly bad approximation as the dimensionality of the system grows larger."

As is well known, the CS EOS for three-dimensional hard spheres[16] plays a prominent role in liquid state theory.[15] While originally derived from the observation that the numerical values of the known virial coefficients came remarkably close to fitting a simple algebraic expression,[16] the CS equation is usually viewed as a suitable linear combination of the compressibility and virial EOS resulting from the PY theory,[15] namely

$$Z_{\text{CS}}(\eta) = \alpha^{(d)} Z_{\text{PY-c}}(\eta) + (1-\alpha^{(d)}) Z_{\text{PY-v}}(\eta) \qquad (4)$$

with $\alpha^{(3)} = \frac{2}{3}$. Since, as it happened in the case $d = 3$, both PY routes keep bracketing the true values in the case $d = 5$,[14] it seems natural to wonder whether the simple interpolation formula (4) works in this case as well. This question was addressed by González *et al.*,[11] who kept the value $\alpha^{(5)} = \frac{2}{3}$. The main goal of this Note is to propose a different choice for $\alpha^{(5)}$. The virial coefficients corresponding to $Z_{\text{CS}}(\eta)$ are $b_n^{\text{CS}} = \alpha^{(d)} b_n^{\text{PY-c}} + (1-\alpha^{(d)}) b_n^{\text{PY-v}}$. By using the known values of b_4–b_6 one gets, however, conflictive estimates for the mixing parameter $\alpha^{(5)}$, namely $\alpha^{(5)} \simeq (b_4 - b_4^{\text{PY-v}})/(b_4^{\text{PY-c}} - b_4^{\text{PY-v}}) \simeq 0.68$, $\alpha^{(5)} \simeq (b_5 - b_5^{\text{PY-v}})/(b_5^{\text{PY-c}} - b_5^{\text{PY-v}}) \simeq -0.02$, and $\alpha^{(5)} \simeq (b_6 - b_6^{\text{PY-v}})/(b_6^{\text{PY-c}} - b_6^{\text{PY-v}}) \simeq 0.40$. On the other hand, minimization of $\sum_{i=1}^{8} [1 - Z_{\text{CS}}(\eta_i)/Z_{\text{sim}}(\eta_i)]^2$ yields $\alpha^{(5)} = 0.62$. By simplicity, here I take the rational number $\alpha^{(5)} = \frac{3}{5}$ and propose the corresponding EOS (4).

Table I compares the MSAV, LM, ASV, and CS EOS with available computer simulations.[5] This table complements Table II of Ref. 14, where Z_{MSAV}, Z_{ASV}, and Z_{CS} (the latter being proposed in this Note) were not included. In general, the accuracy of the EOS with adjusted virial coefficients improves as the degree of complexity increases. More specifically, the average relative deviations from the simulation data are, from worse to better, as follows: 4.7% ($Z_{[3,2]}$), 3.7% (Z_{SMS}), 3.0% ($Z_{[2,3]}$), 2.3% (Z_{BC}), 0.4% (Z_{MSAV}), 0.17% (Z_{LM}), and 0.15% (Z_{ASV}). Concerning the two PY EOS, both are quite poor, with average relative deviations equal to 7.1% ($Z_{\text{PY-v}}$) and 4.2% ($Z_{\text{PY-c}}$). The most interesting point, however, is that the CS-like EOS (4) (with the choice $\alpha^{(5)} = \frac{3}{5}$) presents an excellent agreement with the simulation data (the average relative deviation being 0.3%), only slightly inferior to that of the semi-empirical EOS Z_{LM} and Z_{ASV}. This is especially remarkable if one considers that only the first three virial coefficients of Z_{CS} are exact, a circumstance also occurring in the case of the original CS equation.[16] The choice $\alpha^{(5)} = \frac{2}{3}$,[11] on the other hand, yields an average relative deviation of 0.5%.

Let me conclude with some speculations. It seems interesting to *conjecture* about the existence of possible "hidden" regularities in the PY theory for hard hyperspheres explaining the paradox that, although the virial and the compressibility EOS strongly deviate from each other, a simple linear combination of them *might* be surprisingly accurate. Since the adequate value of the mixing parameter is $\alpha^{(3)} = \frac{2}{3}$ for $d = 3$ and $\alpha^{(5)} = \frac{3}{5}$ for $d = 5$, it is then tempting to *speculate* that its generalization to d dimensions might be $\alpha^{(d)} = (d+1)/2d$,[17] so that $\alpha^{(\infty)} = \frac{1}{2}$ in the limit of high dimensionality, in contrast to other proposals.[13] For $d = 7$ the above implies that, while $Z_{\text{PY-v}}$ and $Z_{\text{PY-c}}$ would dramatically differ, the recipe (4) with $\alpha^{(7)} = \frac{4}{7}$ *could* be very close to the true EOS. The confirmation or rebuttal of this expectation would require the availability of simulation data for $d = 7$, which, to the best of my knowledge, are absent at present.

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TABLE I. Compressibility factor Z as obtained from simulation and from Eq. (1) (MSAV), Eq. (2) (LM), Eq. (3) (ASV), and Eq. (4) with $\alpha^{(5)} = \frac{3}{5}$ (CS, this work)

$\rho\sigma^5$	Simulation[a]	MSAV	LM	ASV	CS
0.2	1.653(1)	1.653	1.653	1.653	1.653
0.4	2.624(3)	2.617	2.618	2.618	2.616
0.6	4.008(6)	4.003	4.009	4.007	4.000
0.8	5.997(11)	5.964	5.986	5.979	5.964
1.0	8.748(16)	8.720	8.770	8.758	8.731
1.1	10.523(20)	10.488	10.553	10.548	10.510
1.15	11.589(22)	11.490	11.560	11.561	11.520
1.18	12.217(24)	12.133	12.204	12.219	12.168

[a]Ref. 5

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[17] Further support for this choice is provided by the case of hard disks. Comparison of numerical solutions of the PY equation with Monte Carlo simulations [D. G. Chae, F. H. Ree, and T. Ree, J. Chem. Phys. **50**, 1581 (1969)] gives average relative deviations of 4.5% ($Z_{\text{PY-v}}$) and 1.0% ($Z_{\text{PY-c}}$), while Eq. (4) with $\alpha^{(2)} = \frac{3}{4}$ yields a deviation of 0.4%.